

CHLOROHYDRINS AND OXIDES OF THE ISOMERIC-2-BUTENES

Thesis by

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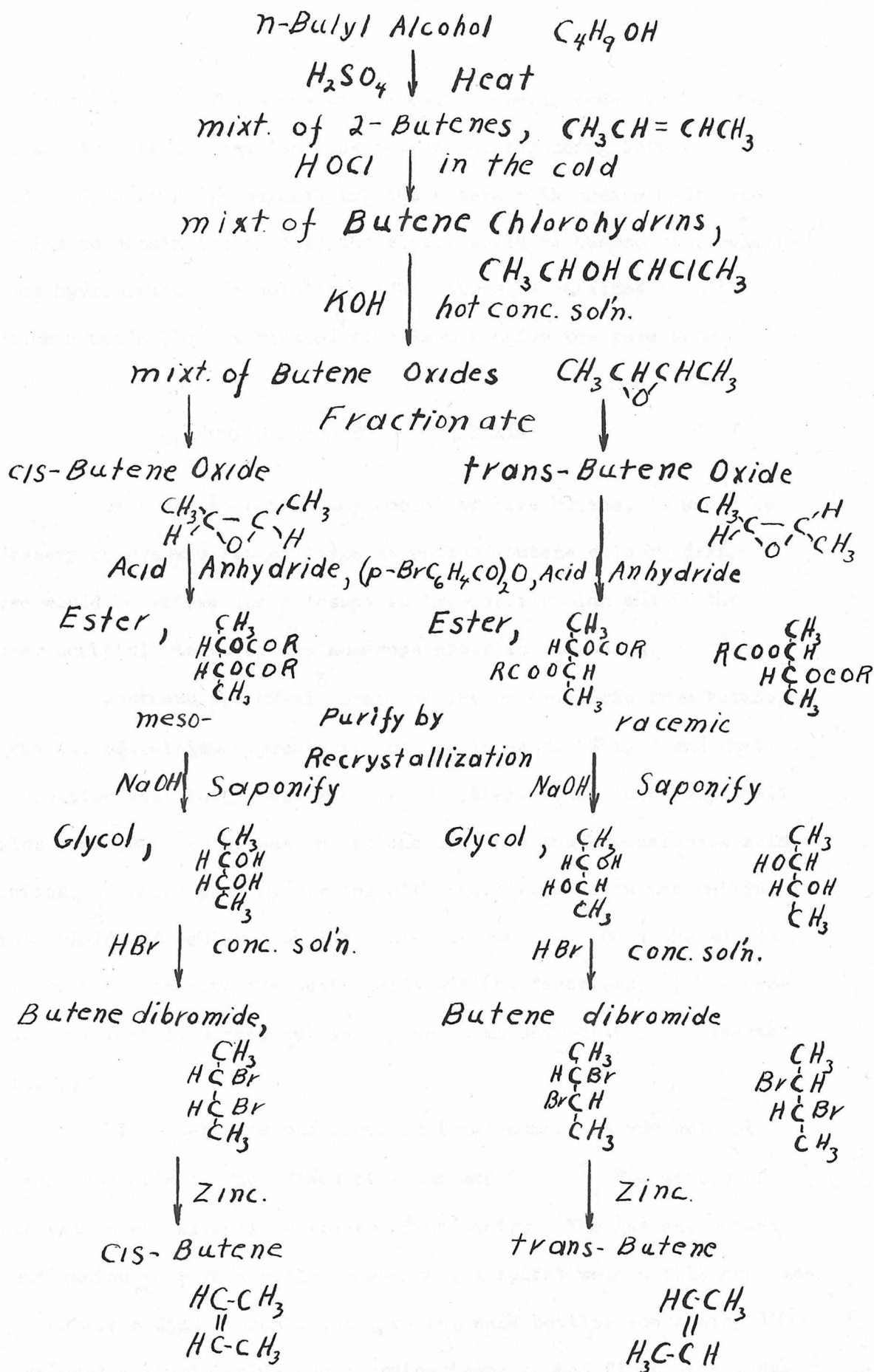
CHLOROHYDRINS AND OXIDES OF THE ISOMERIC 2-BUTENES

INTRODUCTION

The importance of connecting chemical activity and physical properties with the configuration of organic molecules should not be underestimated. The study of the isomeric butenes should be especially illuminating. In these rather simple compounds and the compounds derived from them, we have all of the types of isomerism that are shown by the more complicated molecules. The object of this research is to obtain, from a mixture of cis- and trans-2-butene, the pure isomeric forms by conversion to suitable derivatives which will allow a separation to be made, either through distillation or crystallization methods. It is also desirable to establish the configurational relationships of the butenes and the related compounds. This research would have additional value if it were done by a method that would be applicable to the 2-pentenes. The preparation of isomeric 2-butenes has previously been accomplished by Wislicenus, Talbot, Henze and Schmidt¹ and by Young, Dillon and Lucas⁽²⁾.

The general plan of attack (fig. 1) was to prepare the mixed 2-butenes from n-butyl alcohol with sulfuric acid. Hypochlorous acid was to be added to the double bond to prepare the chlorohydrins. Then by the use of potassium hydroxide, HCl can be pulled out leaving the butene oxides. The oxides were to be subjected to fractional distillation until they were nearly pure. Then each oxide would be separately added to a suitable anhydride. The anhydride would be so chosen that the resulting di-esters of butene glycol would be solids. These solids would be carefully purified by recrystallization. This would constitute

Schematic Plan of Allack (fig.1.)



The relationships suggested are probably not those that actually exist.

the separation into the meso- and racemic isomers; each of these must then be separately converted back to the corresponding butene. This would be done by first saponifying the esters with sodium hydroxide solution to obtain the glycol; the glycol would be heated with concentrated hydrobromic acid solution. The dibromide obtained from this procedure would then be reduced with zinc to give the pure butene.

PREPARATION OF CHLOROHYDRIN

In order to obtain any amount of pure butene, it would be necessary to prepare rather large amounts of butene chlorohydrin. There would be rather large losses in the purification and in the rather doubtful yields of the numerous steps in the chain.

Fourneau and Payal³ prepared the chlorohydrin from butene by the use of calcium hypochlorite and boric acid. They found that the reaction was slow. Last year Mr. W.F. Eberz found that only small yields were obtained by passing butene gas into the hypochlorous acid solution. I found that by working with the liquid below the boiling point, yields of better than 50% could be obtained. Only the method that was found to give the best yields will be described. (This procedure was largely worked out last year as an undergraduate research problem.)

Mixed 2-butene was prepared from commercial 99% butanol and sulfuric acid by the method of Young and Lucas.⁴ The method of purification was slightly different from theirs. The gas was passed in succession through a reflux condenser, a spiral wash bottle containing 3-normal sodium hydroxide, two spiral wash bottles containing 40% (by volume) sulfuric acid, and a drying tower packed first with soda-

lime and then calcium chloride. The gas was then trapped in an ice-hydrochloric acid bath.

The chlorohydrin was prepared in a two-liter three-neck flask. The center neck was provided with a mercury seal stirrer. One of the side necks was used to make connections with a reflux condenser containing alcohol and solid carbon dioxide. The addition of materials could be effected through the other neck. The flask was cooled with an ice-salt bath. Approximately 400-500 cc. of water was added to the flask (just sufficient water to form an easily stirred suspension with the calcium hypochlorite). After the water had cooled, the calculated amount of calcium hypochlorite (H T H 65% available chlorine - 65% $\text{Ca}(\text{ClO})_2$ and 35% NaCl) was added with stirring. It is rather important that the stirring does not stop after the hypochlorite is added because it settles out in a lumpy mass. While the material was cooling down to about -10 to -15° , the reflux condenser was put in place. Then the weighed butene in an ampoule was either boiled or poured through a rubber tube into the reaction flask. After adding the butene a dropping funnel was provided in place of the entrance tube. Glacial acetic acid was added slowly to the mixture until all of the hypochlorite was used up. For example, using 150 grams of butene and the calculated equivalent amount of hypochlorite 3 or 4 hours were necessary for adding the acid. (Some experiment with a modified procedure were carried out in a tin can. With the better heat transfer the addition of the acid took only a half an hour. The yields were not quite as good.) The emulsion that was usually formed was broken up by adding an excess of concentrated nitric acid. The organic phase was removed with the use of a large separatory funnel. The water phase was extracted with 3 or 4 100-cc. portions of isopropyl ether.

The organic phase was added to the ether extract and the two were neutralized with potassium carbonate and dried with calcium chloride. Most of the ether was distilled off at atmospheric pressure through a four-foot Hempel column, fixed so that a vacuum could be used later. (It would not be necessary to use a column this high for this distillation.) The pressure was gradually reduced as the remaining ether and butene dichloride was removed. The product was finally distilled at 30 mm. pressure. The fraction boiling between 50 and 60° was taken. It was necessary to maintain the pressure at this low value because of a high boiling residue of undetermined composition, which raised the boiling point, causing decomposition at higher pressures.

The advantages of the method are that butene is always in excess, the oxidizing action of the hypochlorous acid is reduced to a minimum by using a weak acid, and less free chlorine is produced. By using the liquid butene mechanical losses are practically removed. In some cases yields of 55 to 60% were obtained. A disadvantage is that for a good yield it is only convenient to prepare 150 gms. in a batch. One day is usually required to produce the butene. Another day is necessary to prepare the chlorohydrin and dry it. And part of a third day is required for the distillation. As it was necessary to prepare a large amount of chlorohydrin, this procedure soon became very tedious.

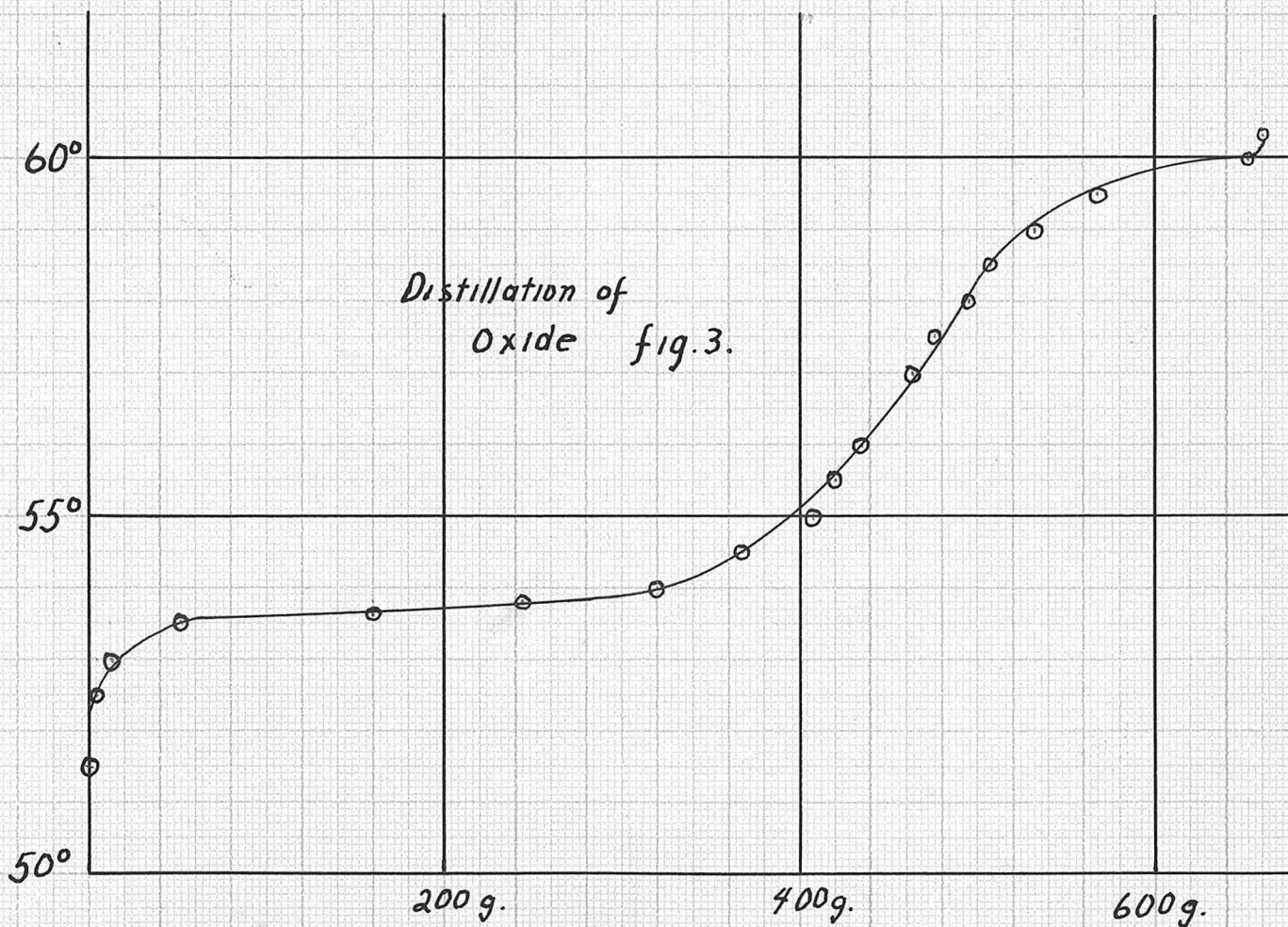
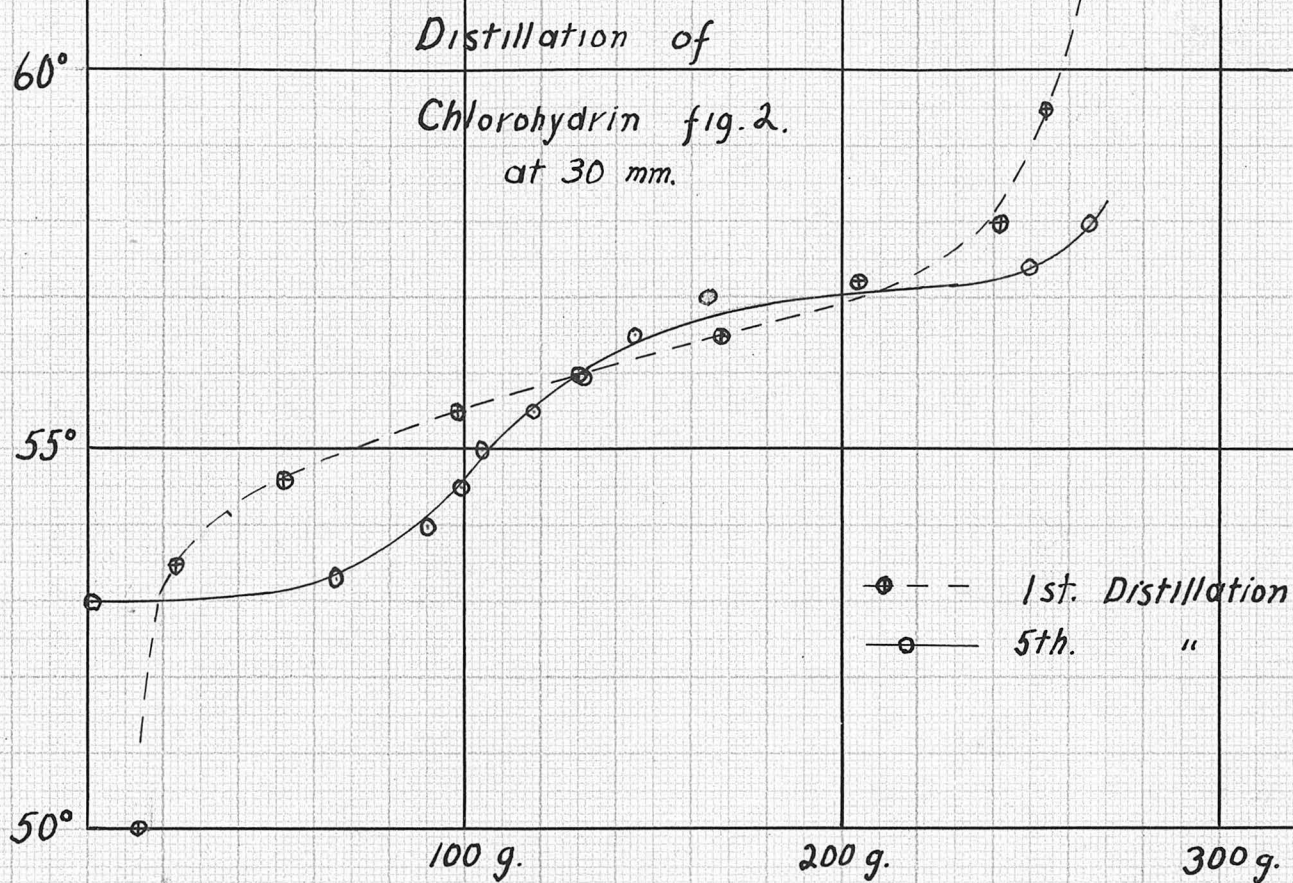
Fractionation of the Isomeric Chlorohydrins of 2-Butene: A portion of the chlorohydrins were subjected to five vacuum fractional distillations (30 mm.). A four-foot Hempel column with a reflux condenser was used. A receiver was employed that permitted the taking of different fractions without interrupting the distillation. Fractions

were taken at approximately every half degree. The distilling flask was provided with a separatory funnel for introducing new fractions at the appropriate time. Diphenyl ether was added at the last of the distillation to serve as a still base for driving over the higher boiling fractions. The results of the first and fifth distillations are shown in fig. 2.

TABLE I. Properties of Chlorohydrin Fractions

	1	2	Beilstein
Bp _{30 mm}	53.0-53.3°	57.0-57.4°	
Bp ₇₄₂	132.0-132.5	135.0-135.5	136-137.5 760
Weight	65.8 gm.	86.0 gm.	
Sp. gr. $\frac{20^\circ}{20^\circ}$	1.0677	1.0685	1.105
Refractive index, $n_d^{20^\circ}$	1.4421	1.4388	1.44376

The densities were determined in a 5-gm. piknometer. The refractive indices were determined in an Abbe refractometer.

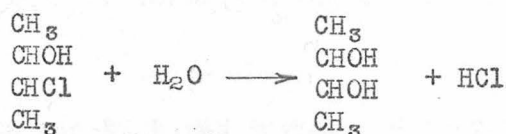


DISCUSSION

It was thought that this would perhaps be a good place to carry out a rough separation. The fact that a constant low pressure is required, together with the fact that there are large losses from decomposition and mechanical loss (only 267 gms. were recovered from 424 gms. = 63%), indicates that the separation could be carried out better at the oxide stage.

Relative Hydrolysis Rates of the Isomeric Chlorohydrins.

It was important to know the order of magnitude of the rate of the reaction:



If the rate of this reaction is large then quite probably large amounts of the chlorohydrin produced would be hydrolysed in the process of preparation. Some of the chlorohydrin was weighed out into a volumetric flask and diluted with water. The hydrochloric acid formed by the hydrolysis was titrated from time to time with standard sodium hydroxide solution. It was found that the reaction was very slow at room temperature. A week was necessary for a few tenths of a cubic centimeter change in the 0.1 normal sodium hydroxide required. This would indicate that if the hydrolysis took place, it would be during the distillation before the water had been entirely removed as a constant boiling mixture with isopropyl ether. Preliminary experiments were made to show that the order of the reaction was that indicated by the equation. It was also found that in basic solution the hydrolysis rate is very fast. If the end point was determined and then a few cubic centimeters of base was

added, the back titration with standard acid was markedly different from the original value. This indicates that the end point must not be over run. This and the fact that the color change of the indicator in the chlorohydrin solution is not sharp makes it extremely difficult to obtain accurate data.

The determination of the hydrolysis rate was made at 75°. The chlorohydrin was weighed out in a weight pipet and diluted with water in a volumetric flask to approximately 0.1 normal. 20 cc. of this solution was pipeted into a number of thin walled test tubes. The test tubes were sealed and placed in a thermostat at 75°. From time to time a test tube was broken in a beaker of water and the extent of the hydrolysis determined.

The rate constant was determined from the following equations:



$$-\frac{d(A)}{dt} = k(A)$$

$$\ln \frac{(A_0)}{(A_t)} = kt$$

Time was recorded in hours, concentration in mols per liter.

TABLE II. Hydrolysis of Chlorohydrin

Time hours	Reaction Rate Constant	
	High boiling	Low boiling
1	0.0555	0.0584
3	-	0.0930
3.5	0.0568	-
7	0.0568	-
8	-	0.0956
12	-	0.0803
13	0.0545	-
22.6	0.0506	-
23	-	0.0892
31	-	0.0800
32.5	0.0490	-
46.6	0.0480	-
47	-	0.0710
102	-	0.0435

The fact that the constant falls off as the reaction proceeds indicates that the samples are impure. The material with the higher rate is hydrolysed first leaving the slower reacting material. The fact that the constants are small indicates that the hydrolysis during the preparation of the chlorohydrin is very small. The fact that the rates are appreciably different for the two isomers may be of interest in determining the configurations.

Preparation of 2-Butene Oxide.

Butene oxide was prepared by Fourneau and Puyall³ by dropping butene chlorohydrin on solid sodium hydroxide. Krasuski⁵ found that it can be prepared either by the action of aqueous potassium hydroxide or lead oxide and water on butene chlorohydrin at room temperature. Neither one of these methods appears to be very satisfactory for making large quantities of butene oxide. With solid sodium hydroxide the surface would soon be covered over with sodium chloride. The reaction at room temperature would be too slow.

The method used was to drop the chlorohydrin on to hot concentrated potassium hydroxide solution. The apparatus consisted of a two-liter three-neck flask provided with a mercury sealed stirrer, a dropping tube, a thermometer, and a short tube leading to a condenser. Several times the calculated quantity of 67% potassium hydroxide solution was used, the chlorohydrin was slowly dropped in and the product distilled out through the condenser cooled by ice water.

TABLE III. Preparation of 2-Butene Oxides

	KOH g.	Chlorohydrin g.	Temp. °C	Time hrs	g.	Yield %
1	20-30 ^a	10	90		3	45
2	500	108	85	1	51	71
3	500	75	70	1/4	34	68
4	1000	327	90	1	202	93
5	1000	409	90	2	246	91
6 } 7 }	2000	853	90	4	497	88

^aPreliminary experiment in small flask

Fractionation of Butene Oxides.

The butene oxides were fractionated through a four-foot Hempel column with a reflux condenser. Fractions were taken at every half degree. The reflux ratio was always greater than ten to one. The distilling flask was provided with a separatory funnel by which fractions could be added at the proper time. Brombenzene was used as a still base for driving over the highest fractions. The oxides were fractionated six times. The results of the sixth distillation are shown in fig. 3. 658 gms. were recovered from the 870 gm. of starting material = 76%.

Table IV. Properties of Oxides.

	1	2	Beilstein
Boiling point ₇₅₀	53.5-54.0°C	59.5-60.0°C	56°
Weight	264 gm.	87 gm.	
Sp.gr. 20°/20°	0.8063	0.8267	
Refractive index n_D^{20}	1.3739	1.3819	

Reaction of Butene Oxide with Calcium Chloride.

After the fifth distillation a small amount of calcium chloride was added to each fraction to remove any water that had been picked up. In all of the fractions of higher boiling point than the center one, a reaction was observed. The calcium chloride especially in the highest boiling fraction became powdery. The powder was separated and the oxide was allowed to evaporate. Then water was added and an oil was formed. Not enough of the oil was produced to be identified. It apparently boiled above 160° with decomposition. It is quite possible that it is butene glycol (b.p. = 180). This seems very interesting that that one isomer should react and the other should not. It might be that this would be a method for separating one isomer into the pure oxide and the other into the pure glycol. I did not investigate this further because the isomer that reacts with calcium chloride is the one that I have the least of. It would be interesting to investigate the nature of the compound formed and the product that results when water is added.

Preparation of p-Brombenzoic Acid and Anhydride.

One of the dibenzoates of butene glycol is reported in the literature⁶ as a solid; the other as a liquid. The 3,5-dinitrobenzoic anhydride would probably give esters with suitable melting points. There is, however, the possibility that in the alkaline solution used for saponifying the esters the nitro group would oxidize the glycol produced. By noting how the melting point is raised or lowered as bromine is substituted in the various positions in the benzene ring in other esters it was concluded that the para-brombenzoic anhydride would be satisfactory. The usual method (described in Beilstein) for making p-brombenzoic acid is to oxidize p-bromtoluene with dichromate in acid solution. Beilstein,

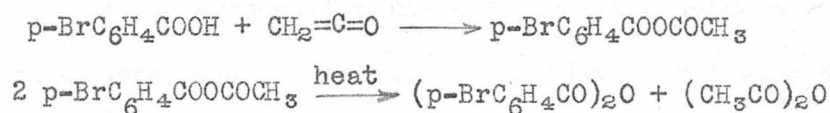
however, does not state how this particular bromtoluene was prepared. Eastman's give the price of p-bromtoluene as \$4 per 100 grams. Since several mols of acid were needed, this would be a rather expensive source. Professor Lucas thought that a method had been described in the literature for preparing para-brombenzoic acid directly by brominating sodium benzoate. This method could not be located, so some experiments were attempted.

The best results were obtained by preparing the sodium salt from benzoic acid and sodium carbonate, adding approximately an equivalent quantity of sodium acetate, to use up some of the HBr formed in the reaction, and evaporating to a pasty mass. Then the calculated quantity of bromine was added and the flask was sealed and heated on a water bath at 80-90° for eight to ten hours. After the reaction mixture had cooled, it was opened and was found to contain considerable gas. Water was added and the product was filtered off without acidifying. It was necessary to recrystallize the product several times to get a good melting point. It was thought that the isomers could be separated by buffering the solution at the appropriate hydrogen ion concentration. The p-brombenzoic acid has the smallest ionization constant and the least solubility of all the isomers. A lot of time was spent in this way, but it seems to be impossible to effect a separation. Apparently equilibrium is not attained. Different conditions were also attempted for the bromination. The best yield obtained was about 10%. Several flasks blew up in the bromination process. The method seems very unsatisfactory.

It was apparent that it would be necessary to resort to the oxidation of p-bromtoluene. Because the price of this material is so high, it was thought that it could be prepared from p-toluidine through

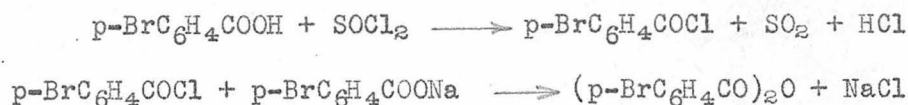
the diazo reaction. This however proved to be unnecessary. On looking up the original method⁷ of preparation described in Beilstein, it was found that the crude ortho-para mixture resulting from the bromination of toluene can be oxidized with chromic acid to yield the pure para-bromobenzoic acid. This method of preparation is very interesting and very satisfactory. It is not necessary to recrystallize the product (m.p. = 250-252). The yield of pure p-bromobenzoic acid obtained from toluene and bromine was 34%, and some toluene was recovered.

The method of Hurd and Dull⁸ for preparing anhydrides was tried. The reactions involved in this method are:



The difficulty arose that p-bromobenzoic ~~anhydride~~ ^{acid} is so slightly soluble in the common solvents that the reaction with the ketene is not very good. Dioxane and acetone are about equally effective as solvents; however, acetone proved to be the best. The reaction was tried at 0°, at room temperature, and at the boiling point of acetone; it is very slow under all of these conditions. It was not necessary to distill the product (it disproportionates into the simple anhydrides in the boiling acetone). Distillation seems undesirable with this anhydride because of the high melting point (218-220°). This method of preparation is not very satisfactory.

The acid chloride was prepared by heating the acid with thionyl chloride. The anhydride was prepared from the acid chloride and the sodium salt by the method of Jackson and Rolfe.⁷ The reactions involved are:



It is questionable which of these methods of preparation is better; perhaps both of them can be improved. The procedure through the acid chloride seems to be more satisfactory.

Preliminary experiments concerning the addition of the anhydride to the butene oxide have been unsuccessful. In the case of the higher boiling oxide there appears to be a reaction with the formation of an ester; the product has not been isolated yet.

I wish to acknowledge the kind help and suggestions of Professor H.J.Lucas, who suggested this problem, and I should like to continue working on it under his direction.

SUMMARY

1. A method is given for the preparation of 2-butene chlorohydrin by the addition of acetic acid to a mixture of calcium hypochlorite and butene at -10°C .
2. A convenient method is given for the preparation of large amounts of butene oxide by dropping butene chlorohydrin on hot concentrated potassium hydroxide solution.
3. The fractional distillation of the isomeric chlorohydrins of the 2-butenes is described.
4. The fractional distillation of the isomeric 2-butene oxides is described.
5. The physical properties of the fractions of 2-butene chlorohydrin and of the fractions of 2-butene oxide are given.
6. The approximate values are given for the hydrolysis rate of the two fractions of 2-butene chlorohydrin.

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